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54 **Addition of aluminium alkyl for improved metallocene catalyst.**

57 The invention is for a catalyst system for polymerization of olefins using an ionic metallocene catalyst with aluminum alkyl. The metallocene catalyst is an ion pair formed from a neutral metallocene compound and an ionizing compound. The invention can be used in any method of producing ionic metallocene catalyst. Use of aluminum alkyl with an ionic metallocene catalyst eliminates the need for using methylaluminoxane (MAO). Catalysts produced by the method of this invention have high activity. The invention reduces catalyst poisons which cause low activity, no activity or uncontrolled polymerizations. Polymerizations using this catalyst system are reproducible and controllable.

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## ADDITION OF ALUMINUM ALKYL FOR IMPROVED METALLOCENE CATALYST

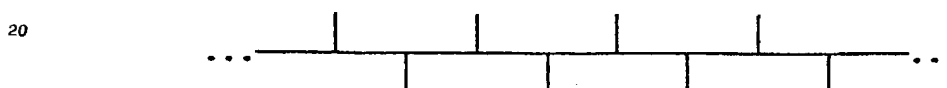
FIELD OF THE INVENTION: This invention relates, in general, to an improved catalyst system and, specifically, to an improved metallocene catalyst system for polymerisation of olefins by addition of an aluminum alkyl and a process for using such a catalyst.

DESCRIPTION OF RELATED ART: Olefins, especially propylene, may be polymerised to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as



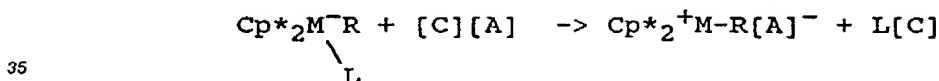
Isotactic polypropylene is capable of being a highly crystalline polymer with a crystalline melting point and other desirable physical properties that are considerably different from the polymer in an amorphous (noncrystalline) state.

A syndiotactic polymer contains principally units of exactly alternating stereo isomers and is represented by the structure:



A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

Polymerisation of olefins is primarily with Zeigler-Natta catalysts. One family of Zeigler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane as a cocatalyst. It has been demonstrated that a Zeigler-Natta catalyst for olefin polymerisation can be formed by combining a Group IV metallocene with an ionic compound.



Cp - pentamethylcyclopentadienyl

M - Group IV metal

R - alkyl

L - ligand

[C] - cation

[A] - anion

The resulting compound is a metal locene cation which acts as catalyst. The cation [C] of the ionic compound reacts with the metallocene to generate an ion pair. The anion, [A], is not coordinated or is only loosely coordinated with the cationic metallocene.

The following methods have been used to produce the above reaction:

One-Electron Oxidation - This method is illustrated in "Ethylene Polymerisation by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex", R.F. Jordan, c.S.Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc., p. 7410-7411, Vol. 108 (1986). These early examples used a Lewis base to make the metal cation less electrophilic and [BPh<sub>4</sub>]<sup>-</sup> was the anion where Ph is C<sub>6</sub>H<sub>5</sub>. The reaction occurred in a solvent which was coordinated with the cation. These materials were usually of low activity.

Protonation - This method is illustrated by "Synthesis and Insertion Reactions of Cationic Alkylbis-(cyclopentadienyl)titanium Complexes", M. Bochmann, L.M.Wilson, J. Chem. Soc. Commun., p: 1610-1611,

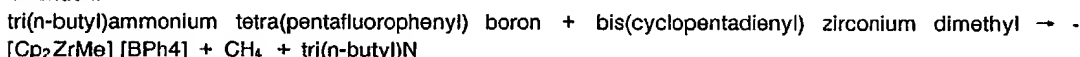
(1986); Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 2556-2563, Vol. 6, (1987); Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes, M. Bochmann, L. Wilson, Organometallics, p. 1147-1154, Vol. 7 (1987).

European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:



where [B] is 7,8-dicarbaundecaborane.

European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:



A by-product of the protonation reaction is a Lewis base (amine) some of which can coordinate to the cations and thus inhibit catalyst activity. Starting materials must be chosen carefully to avoid generating particular amines which are catalyst poisons.

Carbonium Ion Chemistry - This method is illustrated by "Multiple Metal-Carbon Bonds", R. R. Schrock, P. R. Sharp, J. Am. Chem. Soc., p.2389-2399, Vol. 100, No. 8 (April, 2, 1978).

A problem with both the carbonium ion chemistry method and the protonation method is that they are poisoned by basic impurities found in olefins and solvents, often resulting in runaway reactions. The high reaction temperature (over 1000 C) and the short duration of the polymerisation results in short chain lengths and low molecular weight.

Metallocene catalysts are sensitive to poisons in the absence of a scavenging agent, such as methylaluminoxane. Polymerisation requires high concentrations of the cations and frequently end up as either runaway reactions or yield no polymer at all.

## SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for improving metal locene catalyst activity in polymerisation of olefins.

And, it is an object of this invention to use aluminum alkyl as a scavenging agent for poisons which reduce metallocene catalyst activity.

Also, it is an object of this invention to use aluminum alkyl to improve metal locene catalyst activity of a catalyst made by the protonation, carbonium ion chemistry or one electron oxidation method.

Further, it is an object of this invention to reduce cost of a metallocene catalyst system.

Additionally, it is an object of this invention to eliminate methylaluminoxane (MAO) as a cocatalyst in polymerisation of propylene.

As well, it is an object of this invention to produce a metallocene catalyst which affects a controlled polymerization of olefins without a methylaluminoxane cocatalyst.

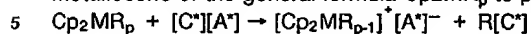
These and other objects are accomplished by mixing an aluminum alkyl with an olefin, preparing a metallocene catalyst then mixing the catalyst with the aluminum alkyl-olefin mixture without a methylaluminoxane cocatalyst. The metallocene catalyst is an ion pair formed from a neutral metallocene compound and an ionizing compound.

## DESCRIPTION OF THE INVENTION

The invention is for a process of polymerising olefins without use of a methylaluminoxane cocatalyst and for a catalyst system for use in such a process. An aluminum alkyl is mixed with an olefin and then introduced into the presence of an ionic metallocene catalyst produced by mixing a neutral metallocene compound with an ionizing agent. Molar ratios for metallocene:ionizing compound:aluminum alkyl range

from 0.5:1:0.5 to 5:1:350 and are preferably from 0.625:1:1.5 to 1.5:1:77 and are most preferably 1:1:1.

In one example of a new synthesis procedure for a metallocene catalyst, an ionizing ionic compound, such as triphenylcarbenium tetrakis(pentafluorophenyl)borate, is mixed with a neutral methyl derivatives of metallocene of the general formula  $\text{Cp}_2\text{MR}_p$  to produce the following reaction:



where Cp is cyclopentadienyl or substituted cyclopentadienyl, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, p is 1 to 4 group,  $\text{C}^+$  is a carbonium, oxonium or sulfonium cation,  $\text{A}^-$  is an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene and  $[\text{C}^+][\text{A}^-]$  is an ionizing agent which does not contain an active proton. Each Cp can be the same or different. Each R can be the same or different. M is preferably titanium, zirconium or hafnium. R is preferably an alkyl, aryl, alkenyl, alkylaryl, or arylalkyl radical of up to carbon atoms and is most preferably methyl.  $\text{Cp}_2\text{MR}_p$  is preferably ethylene bis (tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)-hafnium dimethyl, ethylene bis (indenyl)zirconium dimethyl or isopropyl idene (cyclopentadienyl-1-fluorenyl)-zirconium dimethyl and most preferably ethylenebis(indenyl)zirconium dimethyl. Each reactant is placed in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation, such as methylene chloride or toluene. The preferred solvent is toluene.

The two reactants dissolved separately in the same solvents are mixed together at room temperature. The ionising compound ionises the metallocene and an ion pair is formed in which the metallocene cation acts as a catalyst. After mixing, the mixture is added to an olefin under conditions to effect polymerisation. The olefin is preferably propylene. This procedure is covered by Patent Application Serial No. (reference Attorney Docket Number COS574) which is hereby incorporated by reference into this application.

In another example of a synthesis procedure for a catalyst, two components, the first being a neutral methyl derivative of a metallocene, such as a bis(cyclopentadienyl) metal compound, containing at least one substituent capable of reacting with a proton and the second being an ionic compound with a cat ion capable of donating a proton and an anion which is a coordination complex of a plurality of lipophilic radicals and a metal. The anion is bulky, labile and capable of stabilising the metal cation formed as a result of the reaction between the two compounds. A proton provided by the cation reacts with a ligand of the metallocene. An active catalyst is recovered as a direct product or decomposition product of the reaction. This is the protonation method described above. The above procedure is covered by European Patent Application Publication No. 0-277-004 which is hereby incorporated by reference into this application.

The neutral derivative of the metallocene is of the general formula:

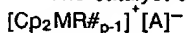


wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal,  $\text{R}'$  is a hydrocarbyl radical, each  $\text{R}'$  being the same or different and p is from 1 to 3. M is preferably titanium, zirconium or hafnium and is most preferably zirconium.  $\text{R}'$  is preferably an alkyl, and aryl an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms. The neutral derivative of the metallocene is preferably ethylene bis (tetrahydroindenyl)zirconium dimethyl or ethylene bis(indenyl)zirconium dimethyl and is most preferably ethylene bis(indenyl)zirconium dimethyl. The ionic compound is preferably N,N-dimethylanilinium tetrakis(pentafluorophenyl) boronate.

In another example of a synthesis procedure for a catalyst, a neutral derivative of a metallocene, such as a cyclopentadienyl metal compound, of the general formula  $\text{Cp}_2\text{MR}''_2$  or  $\text{Cp}_2\text{MR}''\text{X}$  where Cp is cyclopentadienyl or substituted cyclopentadienyl, M is a Group III, IV, V or VI metal, X is a halogen and  $\text{R}''$  is an alkyl combined with a tetraphenylborate metal compound. An  $\text{X}^-$  or  $\text{R}''^-$  is abstracted from the metallocene by the metal of the tetraphenylborate metal compound, resulting in an ion pair of the general formula  $[\text{Cp}_2\text{MR}]^+ [\text{BPh}_4]^-$  where  $\text{BPh}_4$  is a tetraphenyl borate anion.

An aluminum alkyl is mixed with an olefin and brought to reaction temperature. The aluminum alkyl is of the general formula  $\text{AlR}_3$  where R is an alkyl of up to six carbons, preferably trimethylaluminum (TMA) or triethylaluminum (TEA1) and is most preferably triethylaluminum. The olefin is any of the olefins but is preferably propylene or ethylene and is most preferably propylene. The mixture of aluminum alkyl and olefin is brought in contact with a metallocene catalyst. The catalyst may be made by any known method, including but not limited to those described above.

The catalyst system is an ionic metallocene catalyst of the general formula:



wherein  $[\text{Cp}_2\text{MR}\#_{p-1}]^+$  is a metallocene cation wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal,  $\text{R}\#$  is a hydride, a halogen, an amide or a hydrocarbyl radical, each  $\text{R}\#$  being the same or different, except if R is a hydride only one  $\text{R}\#$  is a hydride, p is from 1 to 3 and  $[\text{A}]^-$  is an anion.  $\text{R}\#$  is preferably a hydrocarbyl radical, such

as an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms and is most preferably an alkyl or alkoxy of up to six carbon atoms or an aryl of up to 10 carbon atoms. M is preferably a Group IV metal, such as titanium, zirconium and hafnium and is most preferably zirconium or hafnium. The metallocene cation is preferably a cation of ethylenebis(tetrahydroindenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl, ethylenebis(indenyl)hafnium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl and is most preferably ethylenebis(tetrahydroindenyl)zirconium dimethyl. The anion is preferably tetrakis(pentafluorophenyl)borate. The aluminum is as described above and is most preferably TMA or TEA1 and is most preferably TEA1.

The following metallocene-ionizing agent systems were evaluated with and without addition of an aluminum alkyl:

1.  $\text{Et}(\text{Ind})_2\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
2.  $\text{Et}(\text{Ind})_2\text{HfMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
3.  $\text{Et}(\text{Ind})_2\text{ZrMe}_2/[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$
4.  $\text{iPr}(\text{Cp-1-Flu})\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
5.  $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
6.  $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2/[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$

$\text{Et}(\text{Ind})_2\text{ZrMe}_2$  is ethylene bis(indenyl)zirconium dimethyl,  $\text{iPr}(\text{Cp-1-Flu})_2\text{ZrMe}_2$  is isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl,  $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$  is ethylene bis(tetrahydroindenyl)zirconium dimethyl,  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$  is triphenylcarbenium tetrakis(pentafluorophenyl)boronate,  $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$  is N,N-dimethylanilinium tetrakis(pentafluorophenyl)boronate.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

#### GROUP 1:

##### EXAMPLE I

100 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 10 ml of toluene. 60 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$  was dissolved in 10 ml of toluene. The two solutions were mixed together for 5 minutes at room temperature.

Reactor temperature was set to 50°C and one liter of propylene was pumped into the reactor. The catalyst mixture was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 50°C and the contents of the reactor were agitated for sixty minutes. At the end of the polymerization, the reactor is cooled and the unreacted propylene was vented from the reactor.

The reaction product was dried under vacuum at approximately 40°C for 12 hours. The polymer was then weighed and analysed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

##### EXAMPLE II

The procedure of Example 1 was repeated with the contents of the reactor being agitated for 30 minutes. The results are shown in Table I.

##### EXAMPLE III

The procedure of Example 1 was repeated with the contents of the reactor set point temperature being set at 70°C. The results are shown in Table I.

## EXAMPLE IV

0.32 mmol of trimethylaluminum (TMA) was dissolved in 5 ml of toluene and was added to a 2 liter Zipperclave reactor under 5 psig of nitrogen. Reactor temperature was set to 70°C and one liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

100 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 10 ml of toluene. 60 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub> was dissolved in 10 ml of toluene. The two solutions were mixed together for 5 minutes at room temperature.

The catalyst mixture was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 70°C and the contents of the reactor were agitated for sixty minutes. At the end of the polymerization, the reactor is cooled and the unreacted propylene was vented from the reactor.

The reaction product was dried under vacuum at approximately 40°C for 12 hours. The polymer was then weighed and analyzed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

## EXAMPLE V

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1) and agitating the contents of the reactor for 10 minutes. The results are shown in Table I.

## EXAMPLE VI

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 50 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate and 30 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for 5 minutes. The results are shown in Table I.

## EXAMPLE VII

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 16 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 10 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for ten minutes. The results are shown in Table I.

## EXAMPLE VIII

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for sixty minutes. The results are shown in Table I.

## EXAMPLE IX

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 1.25 mg of Et(Ind)<sub>2</sub>ZrMe<sub>2</sub>. The contents of the reactor were agitated for sixty minutes. The results are shown in Table I.

## EXAMPLE X

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1) - 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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## EXAMPLE XI

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ . The contents of the reactor were agitated for forty minutes. The results are shown in Table I.

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## EXAMPLE XII

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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## EXAMPLE XIII

The procedure of Example II was repeated with 5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 8 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 0.66 mmol of triethyl aluminum and a run time of 30 minutes. The results are shown in Table I.

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## EXAMPLE XIV

The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 8 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 0.66 mmol of triethyl aluminum and a run time of 60 minutes. The results are shown in Table I.

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## EXAMPLE XV

The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 4 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 0.66 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

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## EXAMPLE XVI

The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 4 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 0.99 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

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## EXAMPLE XVII

The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 24 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 0.66 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

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## EXAMPLE XVIII

The procedure of Example II was repeated with 2.5 mg  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 24 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 2.00 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

5 GROUP 2:

EXAMPLE XIX

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The procedure of Example II was repeated with 20 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 80 mg of  $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ , 0.42 mmol of trimethyl aluminum and a run time of 30 minutes. The results are shown in Table I.

15 GROUP 3:

EXAMPLE XX

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The procedure of Example 1 was repeated with 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 7 mg of  $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$ , and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXI

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The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 7.0 mg of  $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$ , 0.66 mmol triethyl aluminum and a run time of 5 minutes. The results are shown in Table I.

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EXAMPLE XXII

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 7.0 mg of N, N-dimethylanilinium tetrakis(pentafluorophenyl)boronate and 2.5 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ . The contents of the reactor were agitated for twenty-five minutes. The results are shown in Table I.

EXAMPLE XXIII

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The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 3.5 mg of N, N-dimethylanilinium tetrakis(pentafluorophenyl)boronate and 1.25 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ . The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

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EXAMPLE XXIV

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The procedure of Example II was repeated with 1.25 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 3.5 mg of  $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$ , 0.66 mmol of triethylaluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXV

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The procedure of Example II was repeated with 0.625 mg of  $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ , 1.75 mg of  $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$ , 0.66 mmol of triethylaluminum and a run time of 60 minutes. The results are shown in Table I.



GROUP 4:EXAMPLE XXVI

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The procedure of Example 1 was repeated with 40 mg of  $iPr(Cp-1-Flu)_2ZrMe_2$ , 60 mg of  $[Ph_3C][BPh^*_4]$  and a run time of minutes. The results are shown in Table I.

10 EXAMPLE XXVII

The procedure of Example 1 was repeated with 60 mg of  $iPr(Cp-1-Flu)_2ZrMe_2$ , 100 mg of  $[Ph_3C][BPh^*_4]$ , and a run time of minutes. The results are shown in Table I.

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EXAMPLE XXVIII

The procedure of Example II was repeated with 60 mg of  $iPr(Cp-1-Flu)_2ZrMe_2$ , 100 mg of  $[Ph_3C][BPh^*_4]$ , 0.16 mmol of trimethylaluminum and a run time of 60 minutes. The results are shown in Table I.

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## EXAMPLE XXIX

25 The procedure of Example II was repeated using 0.48 mmol of trimethylaluminum (TMA), 100 mg of  $[Ph_3C][BPh^*_4]$  and 60 mg of  $iPr(Cp-1-flu)_2ZrMe_2$ , and a run time of 60 minutes. The results are shown in Table I.

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## EXAMPLE XXX

The procedure of Example II was repeated with 20 mg of  $iPr(Cp-1-Flu)_2ZrMe_2$ , 60 mg of  $[Ph_3C][BPh^*_4]$ , 0.16 mmol of trimethylaluminum and a run time of 60 minutes. The results are shown in Table I.

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GROUP 5:

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## EXAMPLE XXXI

The procedure of Example 1 was repeated with 15 mg of  $Et(H_4Ind)_2ZrMe_2$ , 30 mg of  $[Ph_3C][BPh^*_4]$ , and a run time of 60 minutes. The results are shown in Table I.

45

## EXAMPLE XXXII

50 The procedure of Example 1 was repeated with 20 mg of  $Et(H_4Ind)_2ZrMe_2$ , 40 mg of  $[Ph_3C][BPh^*_4]$ , and a run time of 60 minutes. The results are shown in Table I.

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## EXAMPLE XXXIII

The procedure of Example 1 was repeated with 20 mg of  $Et(H_4Ind)_2ZrMe_2$ , 40 mg of  $[Ph_3C][BPh^*_4]$ , and a run time of 5 minutes. The results are shown in Table I.

## EXAMPLE XXXIV

5 The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$ , 8 mg of  $[\text{Ph}_3\text{C}][\text{BPh}_4^-]$ , 0.66 mmol of TEA1 and a run time of 60 minutes. The results are shown in Table I.

GROUP 6:

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EXAMPLE XXXV

15 The procedure of Example 1 was repeated with 50 mg of  $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$ , 40 mg of  $[\text{Me}_2\text{PhN}][\text{BPh}_4^-]$ , and a run time of 120 minutes. The results are shown in Table I.

## EXAMPLE XXXVI

20 The procedure of Example II was repeated with 2.5 mg of  $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$ , 9.2 mg of  $[\text{Me}_2\text{PhN}][\text{BPh}_4^-]$ , 0.66 mmol of TEA1 and a run time of 60 minutes. The results are shown in Table I.

The following results are from the experimental runs described above using the method of the present invention.

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TABLE I

Run #	Catalyst umol (mg)	Ionizing Agent umol (mg)		Al-alkyl mmol	Run Time min.
	Et(Ind) <sub>2</sub> ZrMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]			
1	159(60)	109(100)	TMA TEA1	0	60
2	159(60)	109(100)		0	30
3	159(60)	109(100)		0	60
4	159(60)	109(100)		0.32	60
5	159(60)	109(100)		0.33	10
6	80(30)	54(50)		0.33	5
7	26.5(10)	17.3(16)		0.33	10
8	6.63(2.5)	8.64(8)		0.66	60
9	3.36(1.25)	8.64(8)		0.66	60
10	6.63(2.5)	8.64(8)		0.66	30
11	6.63(2.5)	8.64(8)		0.66	40
12	13.3(5)	8.6(8)		0.33	30
13	13.3(5)	8.64(8)		0.66	30
14	6.63(2.5)	8.64(8)		0.66	60
15	6.63(2.5)	4.3(4)		0.66	30
16	6.63(2.5)	4.3(4)		0.99	30
17	6.63(2.5)	26(24)		0.66	30
18	6.63(2.5)	26(24)		2.00	30
	Et(Ind) <sub>2</sub> HfMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]			
19	53(20)	85(80)	TMA	0.42	30
	Et(Ind) <sub>2</sub> ZrMe <sub>2</sub>	[Me <sub>2</sub> PhN][BPh <sub>4</sub> ]			
20	5.6(2.5)	8.7(7.0)	TEA1	0	60
21	6.6(2.5)	8.7(7.0)		0.66	5
22	6.6(2.5)	8.7(7.0)		0.66	25
23	3.3(1.25)	4.35(3.5)		0.66	30
24	3.3(1.25)	4.35(3.5)		0.66	60
25	1.65(.0625)	2.175(1.75)		0.66	60
	iPr(Cp-1-Flu)ZrMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]			
26	102(40)	65(60)	TMA	0	60
27	154(60)	109(100)		0	60
28	154(60)	109(100)		0.16	60
29	154(60)	109(100)		0.48	60
30	51(20)	65(60)		0.16	60
	Et(H <sub>4</sub> Ind) <sub>2</sub> ZrMe <sub>2</sub>	[Ph <sub>3</sub> C][BPh <sub>4</sub> ]			
31	40(15)	33(30)	TEA1	0	60
32	53(20)	44(40)		0	60
33	80(30)	67(60)		0	5
34	7(2.5)	8.8(8.0)		0.66	60
	Et(H <sub>4</sub> Ind) <sub>2</sub> ZrMe <sub>2</sub>	[Me <sub>2</sub> PhN][BPh <sub>4</sub> ]			
35	133(50)	44(40)	TEA1	0	120
36	7(2.5)	10(9.2)		0.66	60

Run #	Polymerization Temp (°C)	Yield (gms)	Melting Temp (°C)
1	50	19	137
2	50	11	125
3	70	8	126
4	70	270	124
5	70*	340	126
6	70*	432	No Melt
7	70*	260	118
8	70	319	129
9	70	89	132
10	70	117	
11	70*	377	131
12	70	22	132
13	70	51	131
14	70*	357	127
15	70	9	132
16	70	11	134
17	70	149	131
18	70	62	130
19	70	51	131
20	70	-	-
21	70*	106	125
22	70*	405	127
23	70*	434	127
24	70	385	131
25	70	253	131
26	80	2	-
27	70	51	-
28	70*	284	116
29	70*	268	117
30	70*	156	116
31	50	2	142
32	50	35	138
33	120	70	127
34	70	154	115
35	50	50	133
36	70	116	116

\*Exotherm; reaction temperature increased by more than 10°C.

The process described by this invention synthesizes cations which are used as catalysts in olefin polymerization.

The process of making catalysts with this invention produces catalysts having high activity and reduces the by-products which can inhibit catalyst activity. This new synthesis also reduces the catalyst poisons found in the solvents which can inhibit catalyst activity.

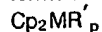
The addition of an aluminum alkyl to ionic metallocene catalyst systems was found to result in reproducible, controllable, high efficiency polymerizations. The addition of an alkyl aluminum provides a scavenging agent for catalyst poisons. The quantity of aluminum alkyl added is relatively small and aluminum alkyls are relatively inexpensive. The metallocene cation/aluminum alkyl combination results in a better catalyst system than the cations alone and give consistently high activities.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

# Claims

1. A process for polymerization of olefins comprising:
  - a) mixing an aluminum alkyl with an olefin;
  - 5 b) preparing a metallocene catalyst;
  - c) mixing the catalyst with the aluminum alkyl-olefin mixture.wherein the aluminum alkyl is of the general formula  $AlR_3$  where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl; and wherein the metallocene is an ion pair formed from a neutral metallocene compound and an ionizing  
10 compound.
2. A process as recited in Claim 1 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.
3. A process as recited in Claim 2 wherein the molar ratio for metallocene:ionizing compound:aluminum alkyl ranges from 0.5:1:0.5 to 5:1:350.
- 15 4. A process as recited in Claim 3 wherein the molar ratio for metallocene:ionizing compound:aluminum alkyl ranges from 0.625:1:1.5 to 1.5:1:77.
5. A process as recited in Claim 4 wherein the molar ratio for metallocene:ionizing compound:aluminum alkyl is 1:1:1.
6. A process as recited in Claim 5 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.
- 20 7. A process as recited in Claim 6 wherein the aluminum alkyl is triethylaluminum.
8. A process as recited in claim 1 wherein the catalyst is prepared by the following steps comprising:
  - a) mixing an ionizing ionic compound with a neutral methyl derivative of a metallocene; and
  - b) allowing contact between the ionizing ionic compound and the neutral methyl derivative of a metalloceneto generate an ion pair in which the metallocene cation acts as a catalyst;  
25 wherein the neutral derivative of a metallocene is of the general formula:
$$Cp_2MR^*_p$$
wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different; M is a Group III, IV, V or VI metal,  $R^*$  is a hydride, a halogen, an amide or a hydrocarbyl radical, each  $R^*$  being the same or different, except only one  $R^*$  is a hydride and p is from 1 to 4;  
30 wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.
- 35 9. A process as recited in Claim 8 wherein the olefin is propylene.
10. A process as recited in Claim 7 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.
11. A process as recited in Claim 10 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.
- 40 12. A process as recited in Claim 11 wherein the M is hafnium or zirconium.
13. A process as recited in Claim 12 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylenebis(tetrahydroindenyl) zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl, ethylene bis(indenyl)hafnium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.
- 45 14. A process as recited in Claim 13 wherein the ionizing ionic compound is triphenylcarbenium tetrakis-(pentafluorophenyl)boronate.
15. A process as recited in claim 1 wherein the catalyst is prepared by the following steps comprising:
  - a) combining, in a suitable solvent or diluent, at least one first compound consisting of a neutral methyl derivative of a metallocene containing at least one substituent capable or reacting with a proton, the metallocene containing a metal selected from the group consisting of titanium, zirconium and hafnium
  - 50 and at least one second compound comprising a cation, capable of donating a proton, and an anion formed as a result of the reaction between the two compounds;
  - b) maintaining the contact in step a) for sufficient period of time to permit the proton provided by the cation of the second compound to react with a ligand of the first compound; and
  - 55 c) recovering an active catalyst as a direct product or as a decomposition product of one or more of the direct products from step b).
16. A process as recited in Claim 15 wherein the olefin is propylene.
17. A process as recited in Claim 16 wherein the neutral methyl derivative of a metallocene is of the general

formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R' is hydrocarbyl radical, each R' being the same or different, and p is from 1 to 4.

18. A process as recited in Claim 17 wherein the M is selected from the group consisting of titanium, zirconium and hafnium.

19. A process as recited in Claim 18 wherein the M is zirconium.

20. A process as recited in Claim 19 wherein R' is selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.

21. A process as recited in Claim 10 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylene bis(tetrahydroindenyl) zirconium dimethyl and ethylene bis(indenyl)-zirconium dimethyl.

22. A process as recited in Claim 21 wherein the first compound is ethylene bis(indenyl)zirconium dimethyl.

23. A process as recited in Claim 22 wherein the second compound is N,N-dimethylanilium tetrakis(pentafluorophenyl) boronate.

24. A process as recited in Claim 1 wherein the catalyst is prepared by the following steps comprising:

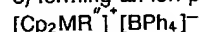
a) combining a cyclopentadienyl metal compound of the general formula



wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, M is a Group III, IV, V or VI metal, X is a halogen and R' is an alkyl combined with a tetraphenylborate metal compound;

b) maintaining the contact in step a) for sufficient period of time to permit abstraction of an X' or a R'-ion from the cyclopentadienyl metal compound by the metal of the tetraphenylborate metal compound; and

c) forming an ion pair of the general formula:



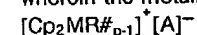
25. A catalyst system comprising:

a) a metallocene catalyst; and

b) an aluminum alkyl;

wherein the aluminum alkyl is of the general formula  $\text{AlR}_3$  where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl.

wherein the metallocene catalyst is an ion pair of the general formula:



aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.

32. A catalyst as recited in Claim 31 wherein the aluminum alkyl is triethylaluminum.